

GRANT
IN 44-CR
164759
P.23

Study of Staebler-Wronski Degradation Effect in a-Si:H based p-i-n Solar Cells

FINAL REPORT

Submitted To

NASA/Lewis Research Center

Grant No. NAG 3-920

Principal Investigators:

H. A. Naseem, W. D. Brown
and S. S. Ang

Department of Electrical Engineering
University of Arkansas
Fayetteville, Arkansas 72701

May 1993



Hameed A. Naseem, Principal Investigator

N93-28406

Unclas

G3/44 0164759

(NASA-CR-193076) STUDY OF THE
STAEBLER-WRONSKI DEGRADATION EFFECT
IN a-Si:H BASED P-I-N SOLAR CELL
(Arkansas Univ.) 23 p

INTRODUCTION:

Conversion of solar energy into electricity using environmentally safe and clean photovoltaic methods to supplement the ever increasing energy needs has been a cherished goal of many scientists and engineers around the world. Photovoltaic solar cells on the other hand, have been the power source for satellites ever since their introduction in the early sixties. For widespread terrestrial applications, however, the cost of photovoltaic systems must be reduced considerably. Much progress has been made in the recent past towards developing economically viable terrestrial systems, and the future looks highly promising. Thin film solar cells offer cost reductions mainly from their low processing cost, low material cost, and choice of low cost substrates. These are also very attractive for space applications because of their high power densities (power produced per kilogram of solar cell pay load) and high radiation resistance. Amorphous silicon based solar cells are amongst the top candidates for economically viable terrestrial and space based power generation.

Despite very low federal funding during the eighties, amorphous silicon solar cell efficiencies have continually been improved - from a low 3% to over 13% now.^[1] Further improvements have been made by the use of multi-junction tandem solar cells. Efficiencies close to 15% have been achieved in several labs. In order to be competitive with fossil fuel generated electricity it is believed that module efficiency of 15% or cell efficiency of 20% is required.^[2] Thus, further improvements in cell performance is imperative.

One major problem that was discovered almost 15 years ago in amorphous silicon devices is the well known Staebler-Wronski Effect.^[3] Efficiency of amorphous silicon solar cells was found to degrade upon exposure to sunlight. Until now there is no consensus among the scientists on the mechanism for this degradation.

Efficiencies may degrade anywhere from 10% to almost 50% within the first few months of operation. In order to improve solar cell efficiencies it is clear that the cause or causes of such degradation must be found and the processing conditions altered to minimize the loss in efficiency.

This project was initiated in 1987 to investigate a possible link between metallic impurities, in particular, Ag, and this degradation. Such a link was established by one of the NASA scientists for the light induced degradation of n⁺/p crystalline silicon solar cells.^[4]

OBJECTIVE:

The objective of this investigation was to study the light-induced degradation (S-W effect) in amorphous silicon solar cells, in particular, to investigate a possible link between Ag impurities and this degradation. Furthermore, the goal was to improve stability and efficiency of amorphous silicon based solar cells.

SUMMARY OF RESEARCH ACCOMPLISHMENTS:

- I. During the first phase of this research the following main results were obtained.
 - a. A single chamber ultrahigh vacuum glow discharge deposition system was built.
A sketch of the system is shown in Fig. 1.
 - b. Deposition parameters for high quality solar cell grade intrinsic silicon (i-Si:H) were optimized using statistical design of experiments methodology. Films with dark conductivities as low as $10^{-10} \text{ S cm}^{-1}$ and photosensitivities better than 5×10^5 were obtained. This work resulted in one M.S. thesis.
 - c. p-i-n solar cells with efficiencies close to 3% were fabricated during first year without any optimization of cell structure.

II. The main achievements during the second phase of research are summarized below:

- a. The p-layer of the p-i-n structure was optimized to couple maximum amount of incoming photon flux into the i-layer for efficient photogeneration and collection. The i-layer thickness was also optimized. These factors resulted in a boost in efficiency to about 8%. This work was included in the second M.S. Thesis that was produced under this project.
- b. In order to improve repeatability in our single chamber system, NF_3 gas line was added to dry etch the system after every deposition. This was done to minimize cross contamination of phosphorus, for example, from a previous run into the boron doped layer.

III. A summary of the work done during the third phase of this project is described below:

- a. The existing thermal evaporator for metallization at U of A was giving unsatisfactory results. Some samples were, therefore, sent to NASA/Lewis for contact metallization. These yielded high efficiencies proving our suspicions about the evaporator.
- b. Internal funding (from the Dean of Engineering) was used to buy and install a new three-source evaporator (Edwards E306A). We have had no contact related problems ever since acquiring this unit. It was found that an evaporation rate greater than $7\text{\AA}/\text{sec}$ was necessary to achieve good quality aluminum for ohmic contacts to a-Si:H.
- c. Etching studies using NF_3 plasma were conducted for a-Si, a-SiN_x and c-Si. This work resulted in a M.S. thesis and a paper at the International Conference on Electronic Materials, Newark, NJ.

- d. Light soaking experiments were carried out by NASA scientists at Lewis Research Center on the first batch of high efficiency p-i-n solar cells (SN5#116). Dark I-V characteristics of cells with Al and Ag metal contacts were compared. No discernible degradation was found in either batch after long exposure to simulated solar illumination. However, many devices got shorted during measurements, possibly due to thin contact layers and sharp probes.
- e. Light induced degradation studies were carried out on p-i-n and n-i-p solar cells at NASA and U of A. The effect of Ag was also studied. The results are briefly discussed in the next section.

Light Induced Degradation of a Si:H Solar Cells:

In order to investigate the effect of Ag impurities in a-Si:H solar cells it was decided to evaporate a thin film ($\sim 30\text{\AA}$) of Ag on SnO_2 coated glass substrates before depositing p-i-n solar cells. It was expected that during deposition Ag atoms will diffuse into the growing film distributing uniformly throughout the cell. Two types of cells were to be fabricated. One, the regular back illuminated p-i-n structure, in which light enters the i-layer through glass substrate and the p-layer. The other, designated as the (front illuminated) n-i-p structure, where light enters from the n-layer side. For the latter devices, transparent conducting oxide (TCO) contacts were to be deposited on the p-i-n a-Si:H cell at Lewis Research Center. These p-i-n and n-i-p structured cells with Ag contamination were to be compared with uncontaminated control devices.

The following devices were fabricated at the U of A and sent to NASA/Lewis for further processing and testing

#P011, no Ag, TCO contact to be deposited at NASA

#P008, 30\AA of Ag, TCO contact to be deposited at NASA

#P012, no Ag, Al contact p-i-n cell

#P004, 30Å Ag, Al contact p-i-n cell

Unfortunately, the person who was to deposit TCO contacts for the n-i-p solar cells left NASA around that time and an attempt to deposit thin transparent Au contacts failed to give continuous films. It was decided at this juncture to try to fabricate (back-illuminated) n-i-p solar cells directly in our deposition system. In other words, we were to deposit n-layer first on SnO_x coated glass substrates which was to be followed by the i- and the p-layers to complete the structure.

As stated earlier, we had optimized deposition parameters and procedure to yield high efficiency (back illuminated) p-i-n solar cells. The back-illuminated n-i-p cells were a new ballgame. Furthermore, it is well known that phosphorus contamination arising from the earlier n-layer deposition causes severe degradation of the intrinsic layer in a single chamber system like ours. Thus, we expected our n-i-p devices to be much inferior to the p-i-n devices obtained under similar deposition conditions.

The p-i-n and n-i-p solar cells fabricated under identical deposition conditions (except the deposition sequence) gave efficiencies of 7% and 1%, respectively. (Later optimization of the n-i-p device resulted in an improvement in efficiency to about 2.5%). These devices with and without Ag contamination (i.e. 30Å of Ag on SnO_x coated glass substrates), were sent to NASA/Lewis where dark characteristics were studied before and after light soaking. The results are shown in Figs. 2, 3, and 4.

It was observed that the p-i-n cells did not show any degradation at all for both Ag contaminated and uncontaminated cells even up to 70 hours of light soaking (Fig. 3). The n-i-p devices, however, showed large degradation after 16 hours of exposure (Fig. 4). It was

furthermore observed that the degradation did not correlate with Ag contamination at all. It could be due either to the inadvertent contamination of the deposition system with Ag that may have poisoned the control cells as well. Or, Ag may not have an observable effect above and beyond what degradation is caused by phosphorus contamination of the i-layer itself. Further research done after thorough scrubbing and chemical cleaning of the chambers still did not provide any conclusive result on this issue. It is also possible that Ag may not have diffused into the i-layer to form impurity-complexes similar to what was observed in crystalline silicon.

Light soaking experiments were also carried out at the University of Arkansas during this period. We report here the effect of various treatments on the efficiency of p-i-n devices SA015 and SA025 (typical behavior) from batch SN5A. The efficiency of cell SA015 was measured to be 7.5% after being stored for few days. After annealing at 160°C for one hour, however, the efficiency improved to 7.8% (state A of i-layer). This cell was mesa etched with NF_3 using Al contact pad as the mask. Surprisingly, the efficiency went up to 8.9%. This improvement could have been due to fluorine passivation of the a-Si:H interface or reduction in surface leakage due to mesa etching and isolation of individual devices. This effect was not investigated further for lack of time and manpower, but is very interesting for improving device efficiencies.

Upon light-soaking under AM1.5 ELH simulated sunlight conditions (100 mW/cm²) the efficiency degraded by about 15% in 60 minutes. Most of this degradation occurred within 20 minutes. The efficiency did not degrade any further upon being left on the shelf for several days. However, it degraded to 5.5% when the cell was annealed at 160°C for one hour in flowing N_2 . A second NF_3 plasma treatment did not bring about any improvement. The degradation of efficiency from 7.2% to 5.5% upon annealing is believed to be due to Al interaction with a-Si:H at these temperatures. Since this interaction masks any improvements in efficiency due to return

to state A of i-layer, thorough investigation was later carried out on Al/a-Si:H interactions at low temperatures. Similar results were observed for SA025. The effect of various treatments on SA015 and SA025 are summarized in Fig.5.

Light-induced degradation and annealing studies on several batches of p-i-n and n-i-p cells were also carried out here at the University of Arkansas. Dark log I-V curves were plotted to measure the effect on dark diode quality factor, reverse saturation current and shunt and series resistances. Fig. 6 shows these curves for a typical p-i-n device (sample #B33 of batch #SN5V). We can see that the series resistance increases upon light exposure. It is also observed that the shunt currents increase upon light soaking as well as annealing. This, we believe, is due to Al diffusion from contacts into a-Si:H.

Fig. 7 shows similar curves for an n-i-p solar cell (sample #NIP-2). Again, it is observed that the diode quality factor, increases upon light soaking. Furthermore, the series resistance is found to increase upon light exposure and decrease upon annealing. One unusual feature observed in the logI-V curve is the shift in the curve upon annealing. Currently, we do not know the reason for this behavior.

Fig. 8 shows diode quality factor (n), series resistance and reverse saturation current plotted as a function of light soaking and annealing for both p-i-n and n-i-p solar cells. It is observed that n-i-p cells have better (smaller) n -values (1.2 in state A), as compared to p-i-n devices (1.7 in state A), although the former cells have much lower efficiencies ($\sim 1\%$) than the latter ($\sim 7\%$). We believe that it is due to inadvertent phosphorus doping of the i-layer which results in a single $p^+-i(v)$ junction in the n-i-p cell in contrast with two junctions (p^+-i and n^+-i) in the p-i-n cells. Fig. 9 shows possible electronic energy band diagrams for the p-i-n and n-i-p structures fabricated in our single chamber system. The voltage applied across each junction of

the p-i-n cell is divided by two, effectively giving it a diode quality factor close to 2 rather than 1. Such a device gives higher efficiency because of higher collection of photogenerated carriers despite its higher apparent diode quality factor. N-i-p cells are also observed to have 20 to 30 times higher series resistance as compared to the p-i-n cells.

Introduction of Ag into the n-i-p and p-i-n cells did not show any discernible differences except that the efficiencies were slightly lower for the Ag-doped cells. It is possible, as stated earlier, that Ag may not have diffused into the i-layer during deposition. Or, the effect may have been severely masked due to the low quality i-layers deposited in our single chamber system in the n-i-p configuration. It was therefore, decided to try to acquire the capability of depositing transparent conducting oxide here at the University so that high efficiency n-i-p cells could be used for this study.

IV. A summary of the work done during the fourth phase of the project is described below:

- a. Since the quality of the back-illuminated n-i-p devices could not be improved in our single chamber deposition system for reasons described earlier we planned to develop the capability to deposit transparent conducting oxide (TCO) coatings here at the university to obtain high efficiency front illuminated n-i-p devices. Two approaches were used: 1) Spray pyrolysis to deposit indium-doped zinc cadmium oxide (ZnCdO) films on a-Si:H at temperatures below 250°C. 2) Magnetron sputtering of indium tin oxide (ITO) films using a two-inch sputter gun.

Spray deposited films of varying Zn and Cd composition and resistivities were deposited and optimized on glass substrates. However, the film quality was extremely poor at deposition temperatures below 250°C. Above this temperature a-Si:H cells lose hydrogen resulting in severe degradation of the device. Thus

spray pyrolysis of ZnCdO could not be used to form the transparent conducting contact for the front illuminated n-i-p solar cells.

The Perkin Elmer Randex 2400 rf diode sputtering unit was retrofitted for a magnetron sputter gun using two-inch indium tin oxide (10% In) target. Oxygen line was added to the inlet manifold. Several films were made at various deposition pressures, d.c. powers and oxygen flow rates. However, the quality of the deposited films could not be optimized for the n-i-p solar cells because of the lack of substrate heater in the J-arm. Such a modification required up to \$10K which was not available. This severely restricted our ability to form high quality n-i-p devices at the university for further light soaking experiments.

- b. A non-reversible degradation in p-i-n devices was observed in our light soaking/annealing experiments. We suspected interaction between Al contact and n-Si:H at relatively low temperatures. A full investigation of Al/a-Si:H interaction resulted in an M.S. Thesis and a paper at Materials Research Society Meeting. Another journal paper is under preparation.
- c. In order to increase device efficiency and stability we introduced NF_3 into the gas phase to fabricate fluorinated a-SiN_x alloys for p-type window layers of the p-i-n solar cells. It was found that the deposition efficiency was improved by several hundred percent and thermal stability of the film also improved substantially. Boron-doping of the fluorinated nitride film resulted in much smaller narrowing of the bandgap than is observed in pure a-Si:H. Hydrogen dilution was also found to improve film quality. Excellent p-i-n devices were fabricated using p-type a-SiN_x:F₂H window layers. Efficiencies in excess of 8% were reported. These

results were presented at MRS Meetings. This research was part of the Ph.D. work done by Mr. Freddie Goh in which he studied wide bandgap amorphous silicon-nitride-carbide alloys for device applications.

- d. Highly conducting doped microcrystalline/crystalline films were fabricated using high power and high hydrogen dilution. Such films are used to increase device efficiencies by replacing highly absorbing a-Si p- and n-layers with less absorbing crystalline films. This work resulted in an M.S. thesis and a paper at the American Vacuum Society Meeting.

PRESENTATIONS AND PUBLICATIONS:

Several conference presentations, proceedings papers and journal articles resulted from this investigation. Five M.S. theses and one Ph.D. dissertation were produced during the tenure of this project (wholly or partially funded by this grant).

Publications/Presentations:

1. "Optimization of Boron Doping for a-Si:H p-i-n Solar Cells," Kin Ng, Freddie Goh and H. Naseem, Sectional Meeting of the American Physical Society (Texas Section), Nov. 1988, Lubbock, TX.
2. "Plasma Etching of Silicon using NF_3 Diluted with Ar, N_2 and H_2 Gases," S.M. Tan, F.H.C. Goh, H.A. Naseem and W.D. Brown, Proc. Int. Conf. Electr. Mat., Vol. IECM-2, p.439-44, 1990.
3. "Fluorinated Silicon Nitride (a-Si:N,F,H) Films using NF_3 for Amorphous Silicon based Solar Cells," F.H.C. Goh, S.M. Tan, H.A. Naseem, W.D. Brown and A.M. Hermann, Proc. Mat. Res. Soc. Symp. Amorphous Silicon Technology, Vol. 192, p. 75-80, 1990.

4. "Wide Bandgap Fluorinated Silicon-Carbide-Nitride Films using NF_3 ," H.C. Goh, S.M. Tan, H.A. Naseem, and W.D. Brown, Proc. Mat. Res. Soc. Symp. Amorphous Silicon Tech., Vol. 219, p. 763-68, 1991.
5. "Hydrogenated Amorphous Silicon/Aluminum Interaction at Low Temperatures," M.S. Haque, H.A. Naseem, W.D. Brown and S.S. Ang, Proc. Mat. Res. Soc. Symp. Amorphous Silicon Tech., Vol 258, p. 1037, 1992.
6. "Highly conductive Silicon Films Via Plasma-Enhanced Chemical Vapor Deposition at Low Temperatures," A.S. Mauskar, H.A. Naseem, W.D. Brown, and S.S. Ang, J. Vac. Sci. Tech. A, Vol. 11, No. 4, (July/Aug.) 1993.

M.S. Theses and Ph.D. Dissertation:

1. "Optimization of Deposition Parameters for Solar Cell Grade a-Si:H Films using Ultra-High Vacuum RF Glow Discharge Technique," M.S. Thesis, Mr. F.H.C. Goh, 1989.
2. "Fabrication of High Efficiency Amorphous Silicon Solar Cells using PECVD," M.S. Thesis, Mr. K.K. Ng, 1989.
3. "Plasma Etching of Silicon, Silicon Nitride and Amorphous Silicon using Nitrogen Trifluoride," M.S. thesis, Mr. S.M. Tan, 1990.
4. "Interaction of Aluminum with Hydrogenated Amorphous Silicon at Low Temperatures," M.S. Thesis, Mr. M.S. Haque, 1992.
5. "Highly Conductive Silicon Films using PECVD," M.S. Thesis, Mr. A.S. Mauskar, 1992.
6. "Wide Bandgap Amorphous Silicon Based Alloys using PECVD," Ph.D. Dissertation, Mr. F.H.C. Goh, 1992.

SUMMARY AND CONCLUSION:

Two clear objectives were defined for this project. First, to study light-induced degradation of a-Si:H based solar cell and to investigate a possible link between Ag impurities and this degradation. Second objective was to find ways to improve efficiency and stability of these devices.

Light-induced degradation was studied for the p-i-n devices here at the U of A and at NASA/Lewis. These devices were found to be very stable under moderate light exposures. Despite our best efforts, however, the n-i-p devices of similar quality and efficiency could not be fabricated for light-soaking studies. This severely limited the scope of the investigation. n-i-p cells were considered important because of their similarity to the n⁺/p crystalline Si solar cells in which NASA scientists had linked the photoinduced degradation to Ag contamination.

Our efforts to improve stability and efficiency of these devices were very successful. Statistical design of experiments was used to optimize various deposition parameters and procedures to yield high efficiency solar cells. NF₃ etching was found to result in a boost in efficiency. Fluorinated a-SiN_x films were deposited for thermally stable widegap windows. Aluminum was found to interact strongly with a-Si:H film at temperatures in excess of 180°C in flowing N₂. Shunt resistances were seen to be affected at even lower temperatures. Highly conducting textured doped layers were formed under high hydrogen dilution and high power deposition conditions. Such window layers are more transparent than their amorphous counterparts. At the heel of this project we initiated several studies on a-Si:H based multijunction solar cells under DOE sponsorship which are expected to yield high efficiencies and low light-induced degradation.

REFERENCES:

1. D. Carlson, IEEE Trans. Electr. Dev., Vol. ED-36, No. 12, p. 2775 (1989).
2. A. Catalano, J. Newton, and A. Rothwarf, IEEE Trans. Electr. Dev., Vol. ED-37, No. 2, p. 391 (1990).
3. D. Staebler and C. Wronski, Appl. Phys. Lett, Vol. 31, p. 292 (1977).
4. V. G. Weizer, H. Brandhorst, J. Broder, R. Hart, and J. Lamneck, J. Appl. Phys., Vol. 50, p. 4443 (1979).

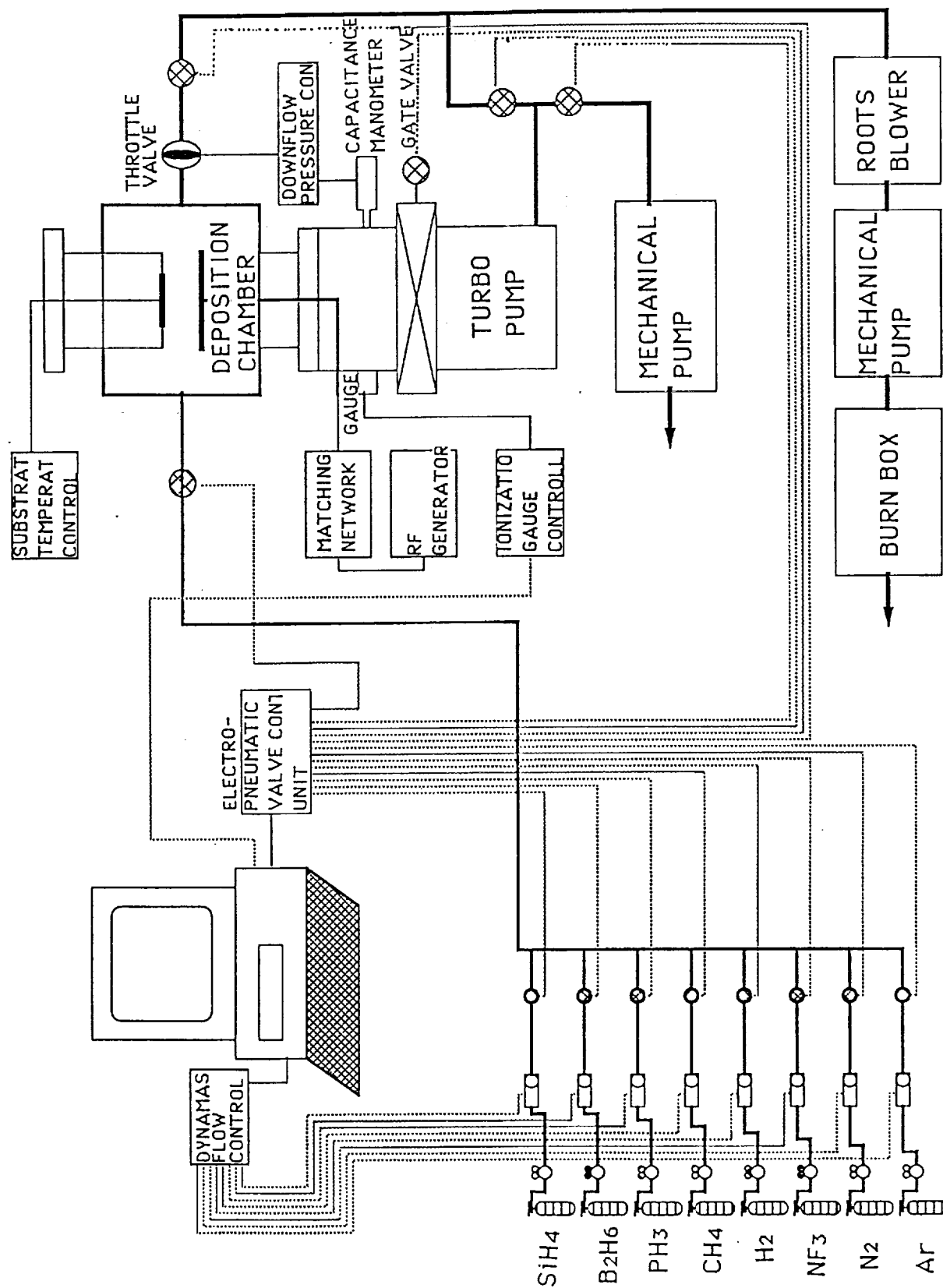
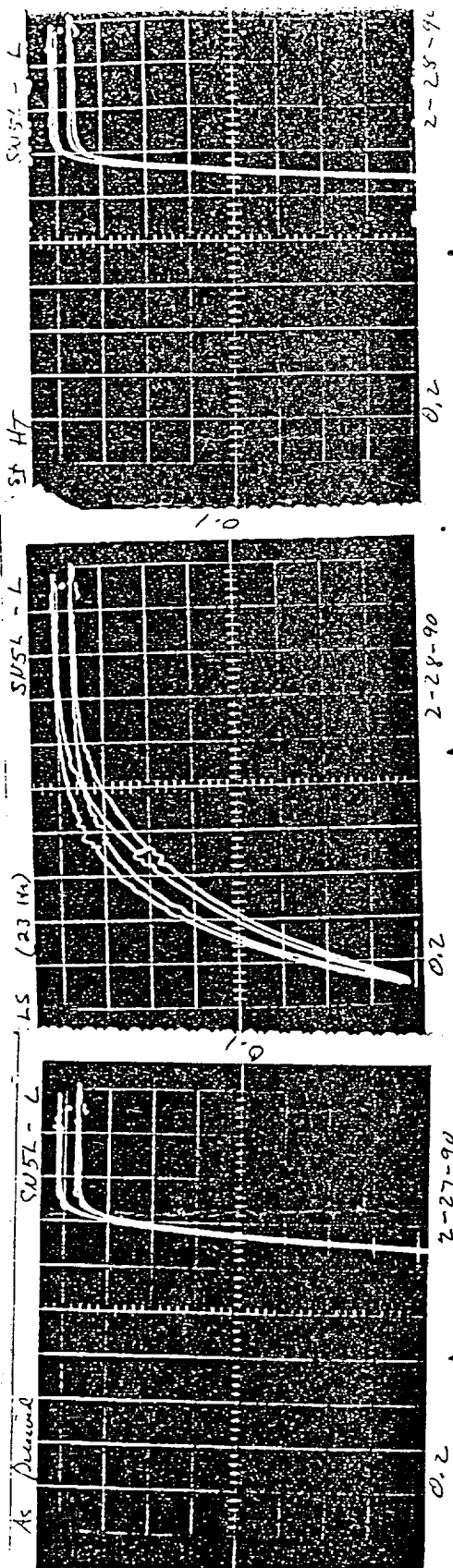


Fig. 1. University of Arkansas ultra-high vacuum plasma enhanced chemical vapor deposition System.

NIP Device



a) As received

b) After 23 hr of light soaking

c) After 25 min of annealing at 180 C

PIN Device

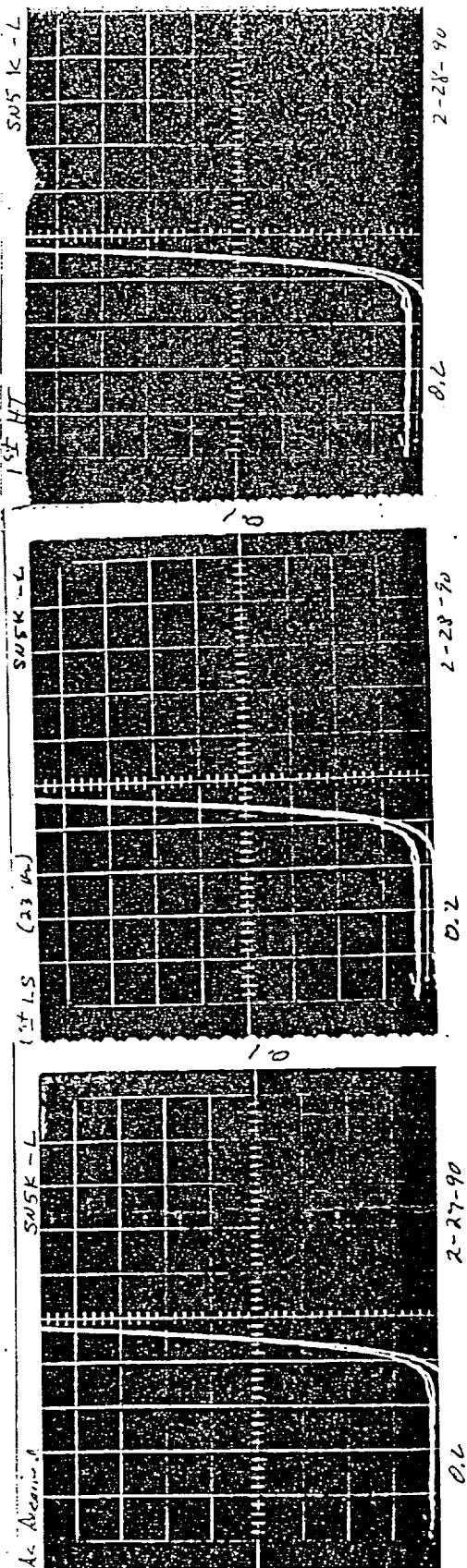
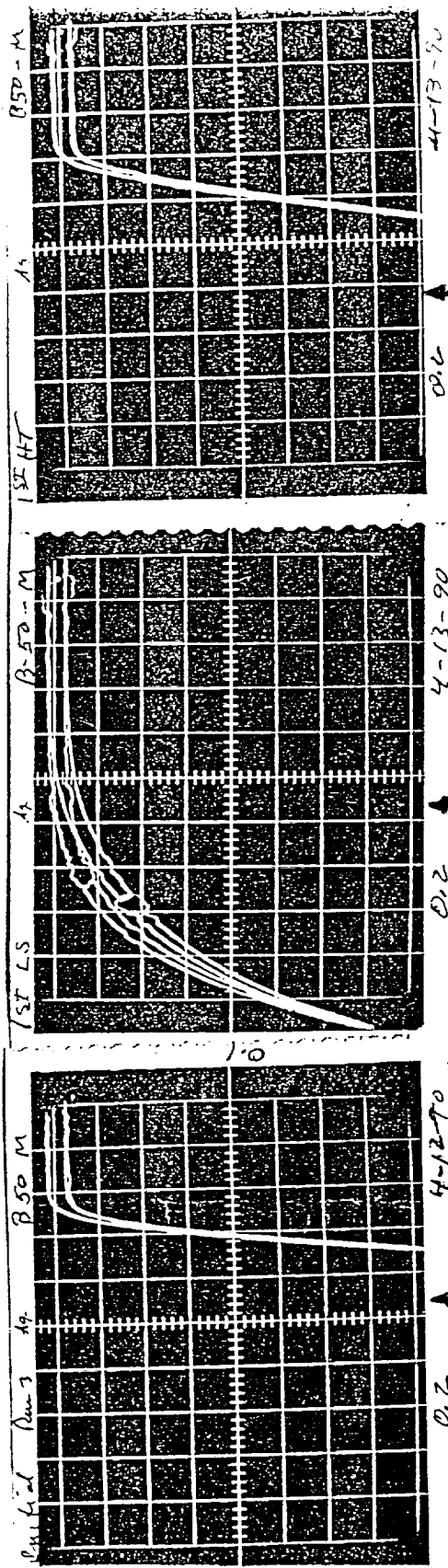


Fig. 2. Dark characteristics of NIP and PIN devices before/after light soaking/annealing

Ag Doped NIP Device



No Ag NIP Device

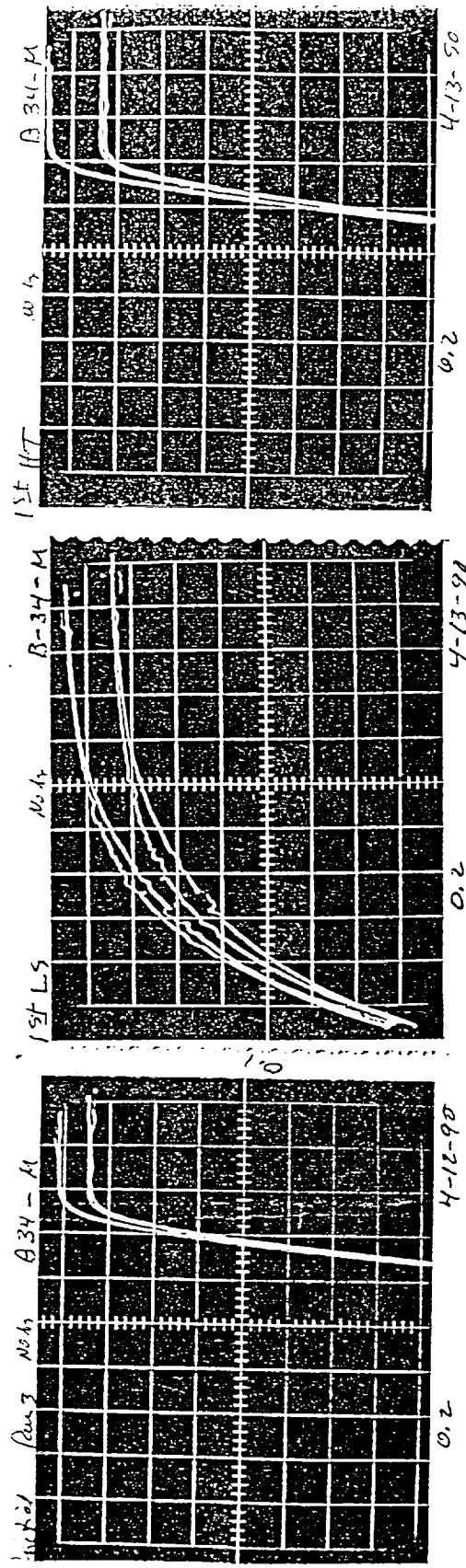


Fig. 4. Dark characteristics of Ag-doped/undoped NIP devices before/after lightsoaking/annealing.

Solar Cell Efficiency SA015 and SA025

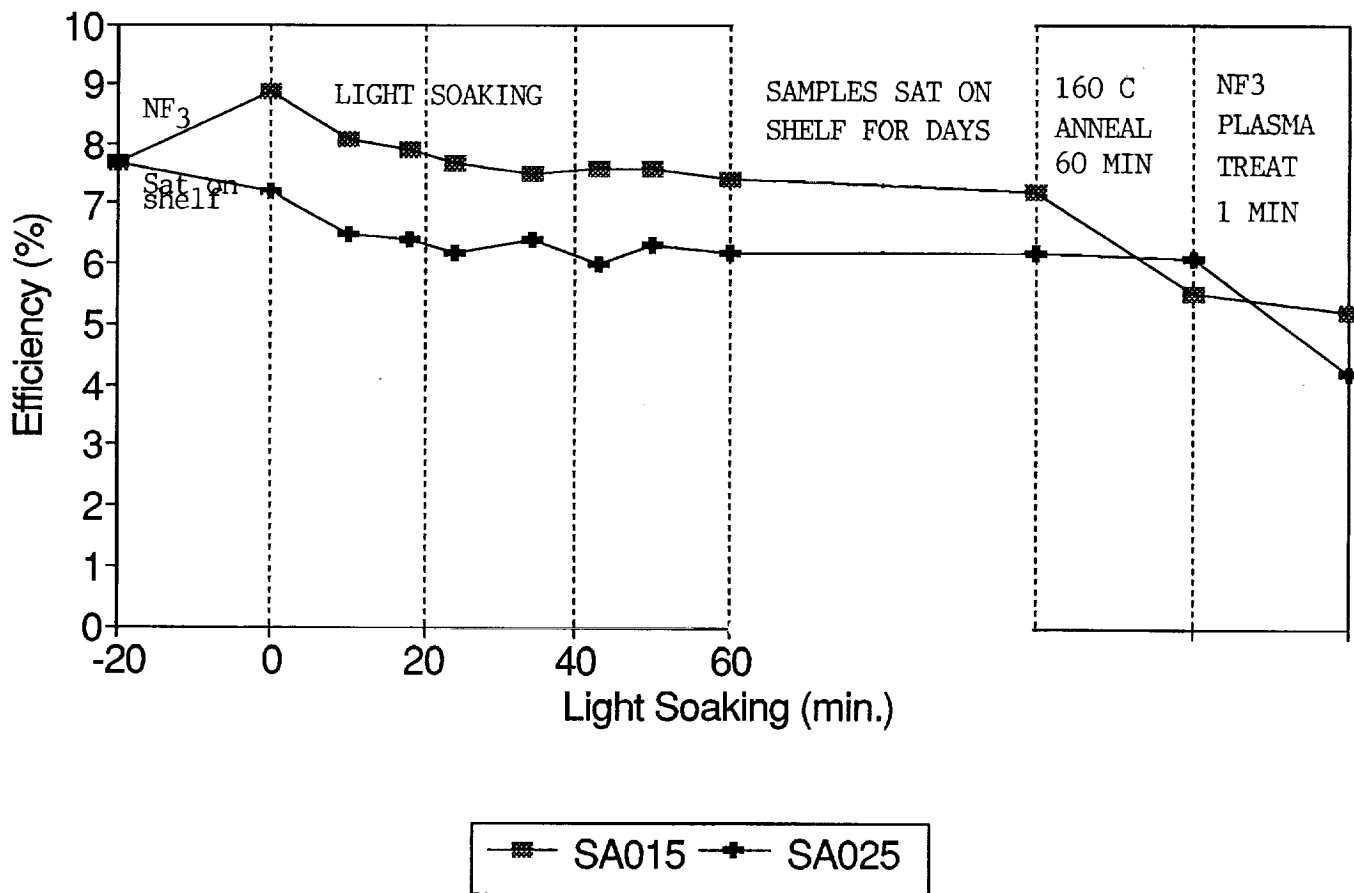


FIG. 5. Effect of NF3 treatment, light soaking and annealing on the efficiency of PIN solar cells.

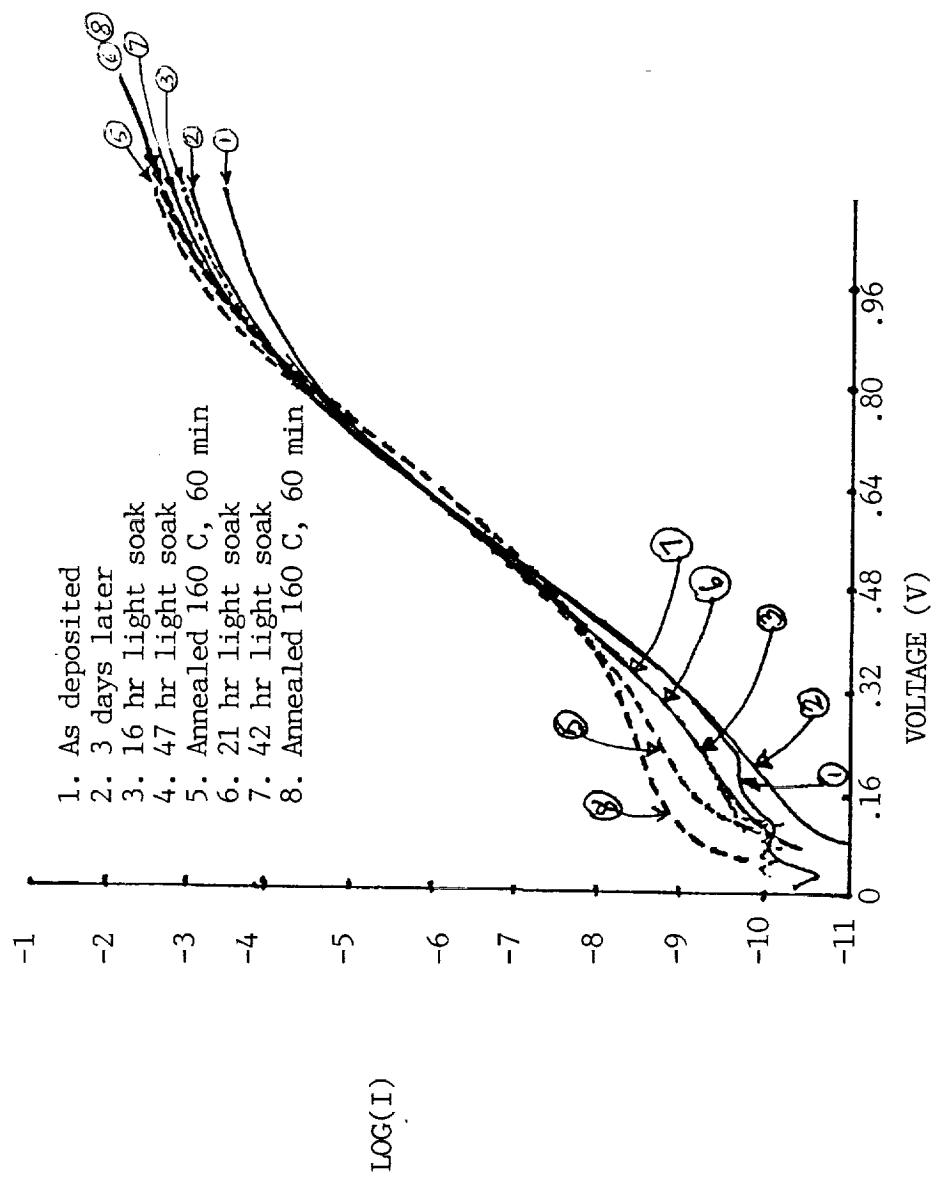


Fig. 6. LogI-V characteristics (dark) of a typical PIN device before/after light soak/anneal.

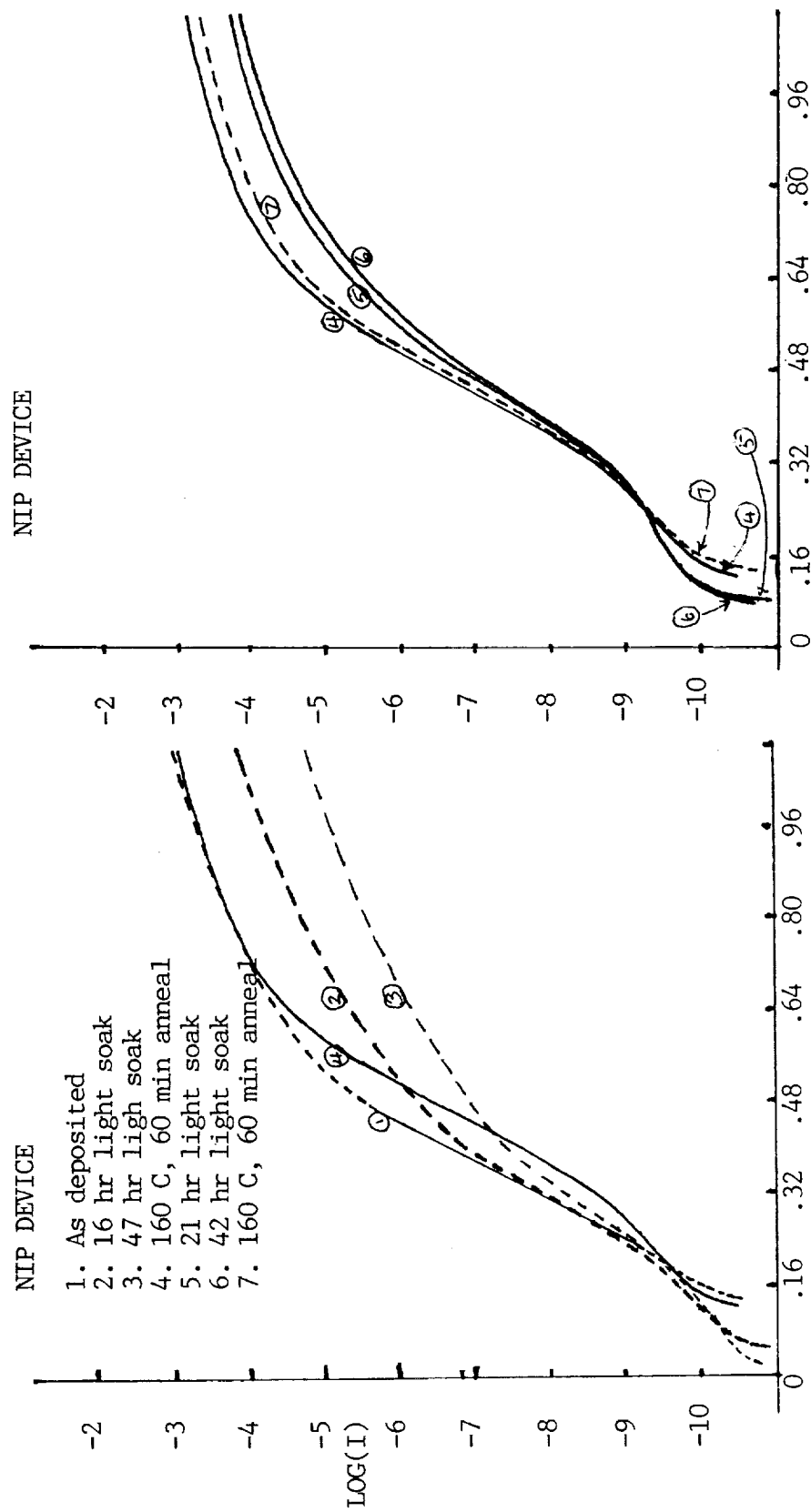


Fig. 7. Log(I)-V Characteristics (dark) of a typical NIP device before/after light soak/anneal.

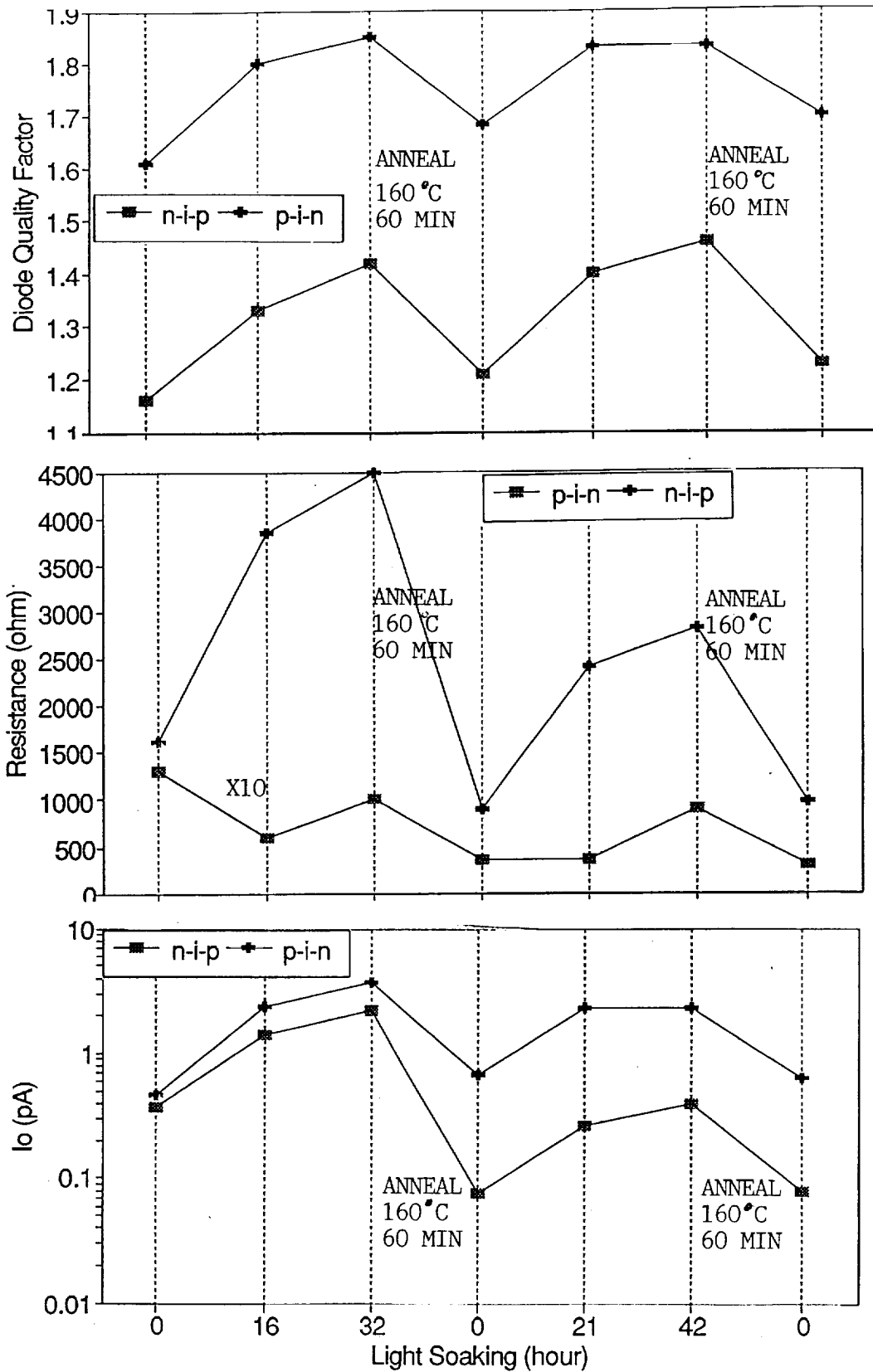


Fig. 8. Diode quality factor (n), series resistance, and reverse saturation current of typical PIN and NIP devices vs. light soaking/annealing.

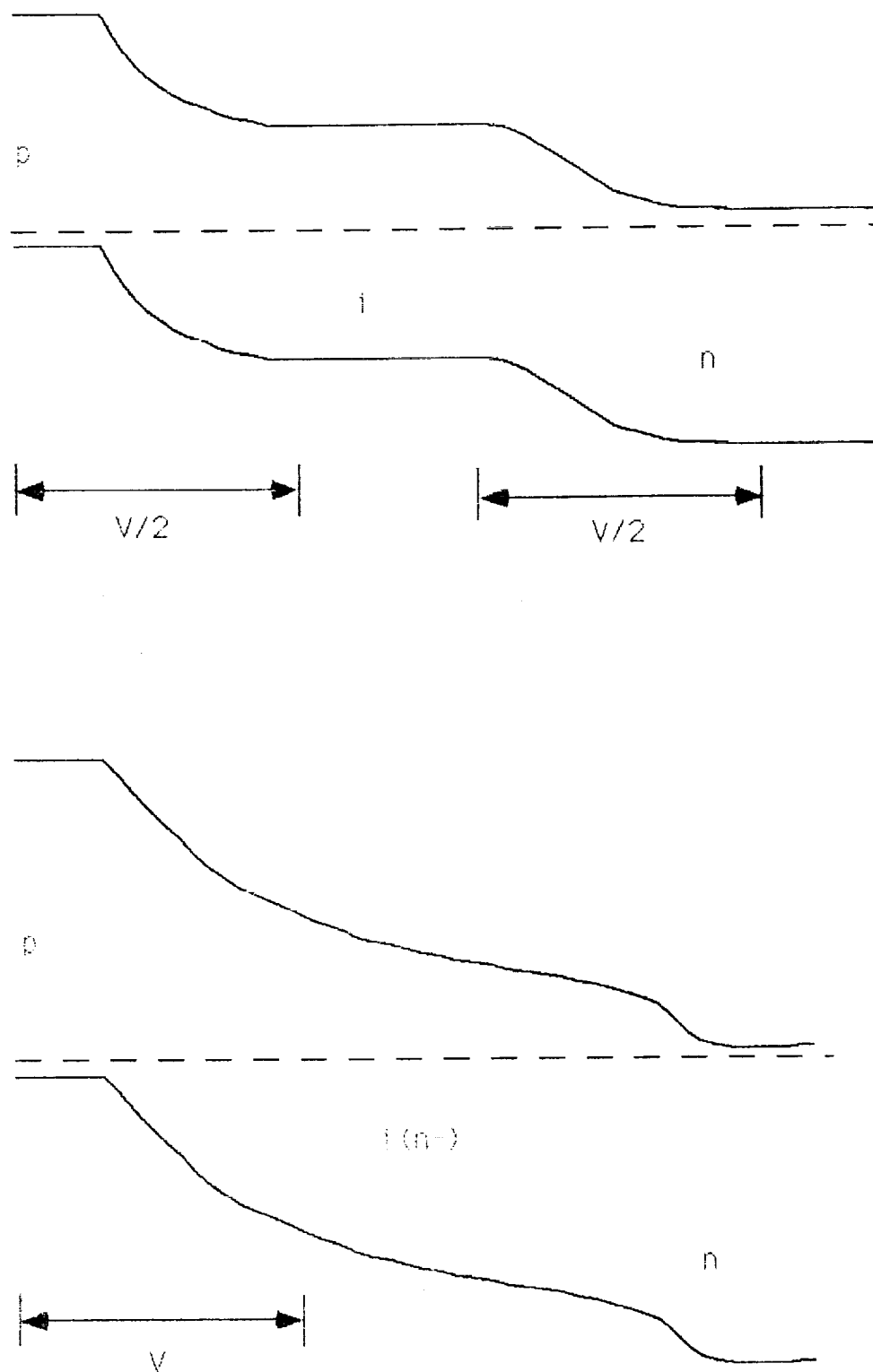


Fig. 9. Expected electronic energy band diagram of back illuminated PIN and NIP devices. Notice the graded n-type doping of i-layer in the NIP device.